

Relationship between resist outgassing and activation energy for EUV and EB



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Outline

- Introduction
- Objective of this work
- Experiment & result
 - ✓ Relation between the outgassing and the activation energy of the protecting group
 - ✓ Relation between the outgassing and the quencher loading
- Summary

Outline

■ Introduction

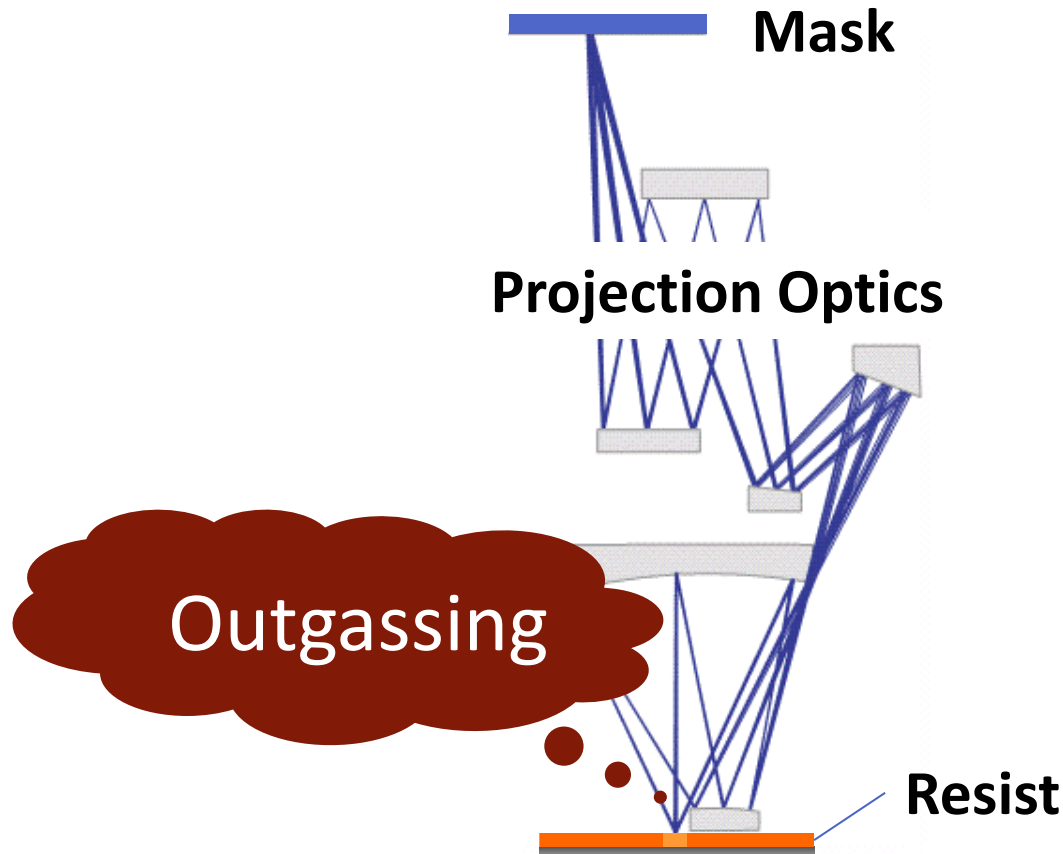
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- ✓ Relation between the outgassing and the activation energy of the protecting group
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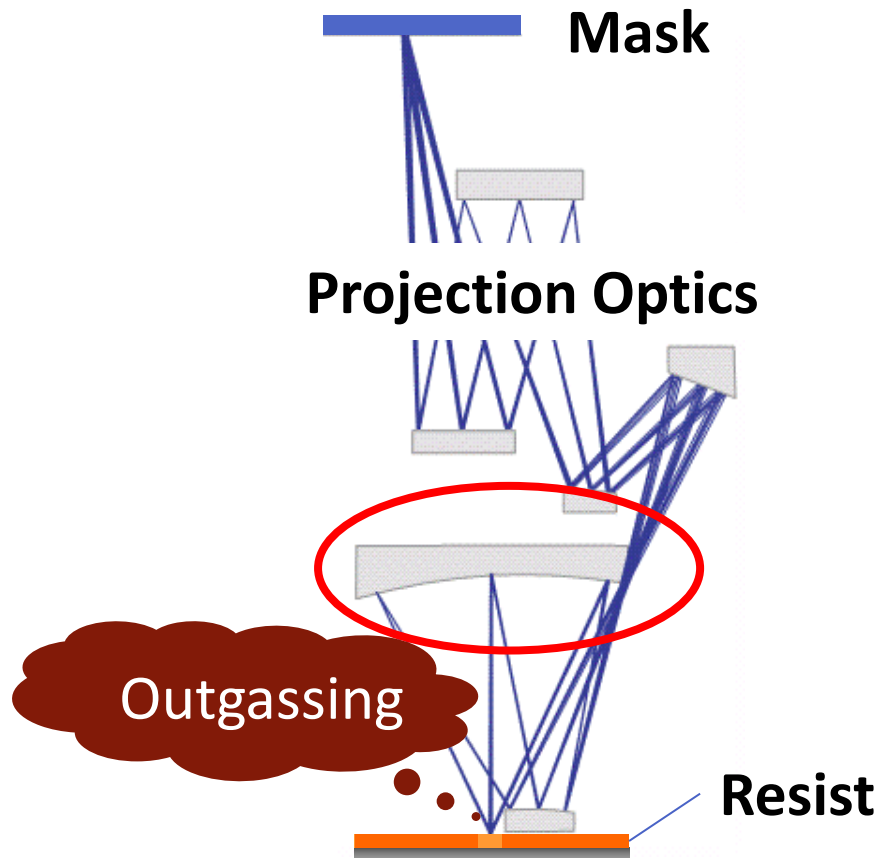
■ Summary

Resist-induced Optics Contamination



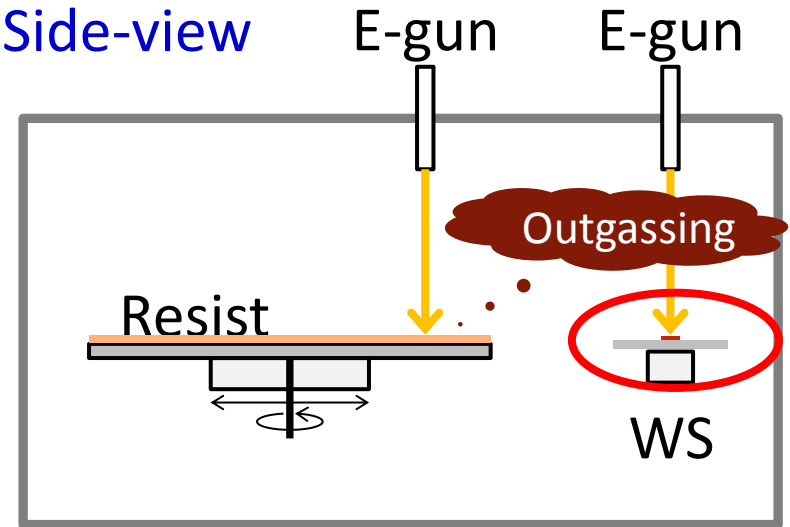
- Outgassing from EUV resist will result in optics contamination.
- Before resists can be used on the EUV scanner, testing by witness sample (WS) method is necessary.

Process Flow of Outgassing Test (WS Method)

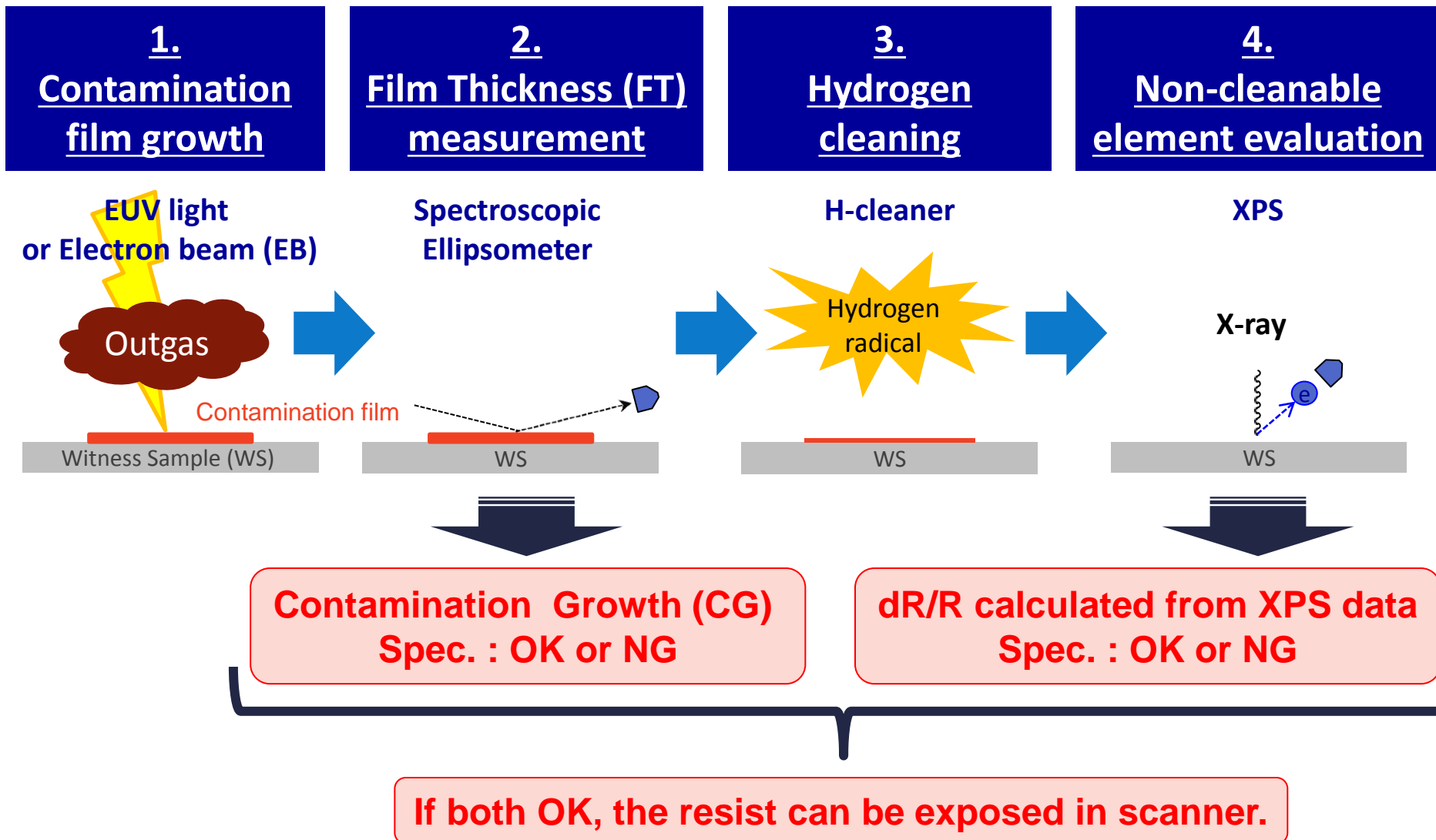


Ex) EUVOM-9000

Side-view



Process Flow of Outgassing Test (WS Method)



Outline

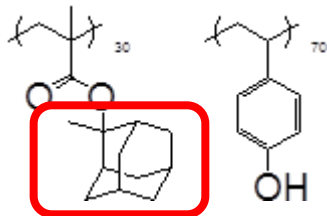
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Objective of This Work

- Clarify the relationship between outgassing and the protecting group.
 - ✓ Size of protecting group
 - ✓ Activation energy (E_a) for de-protection

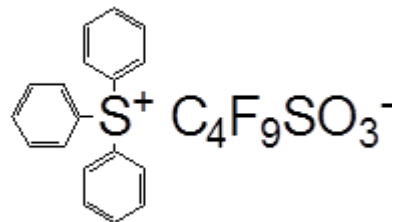
Ex.) Components of model resist

Base resin

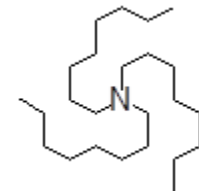


Protecting group

PAG



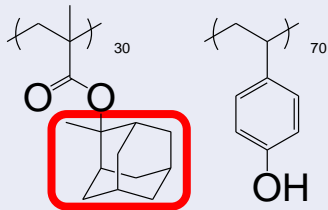
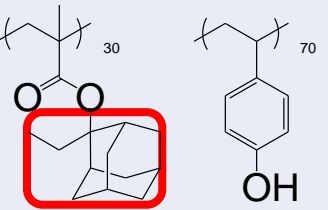
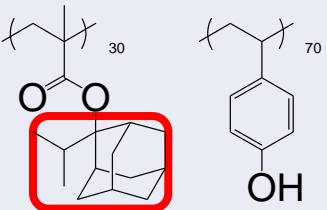
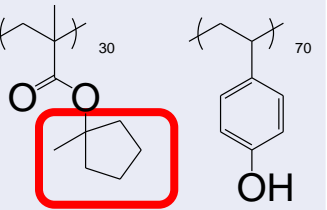
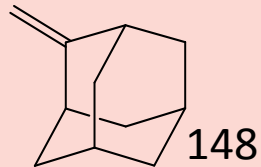
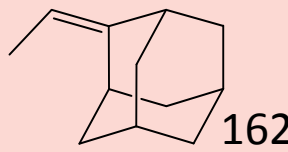
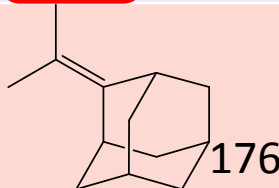
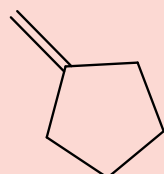
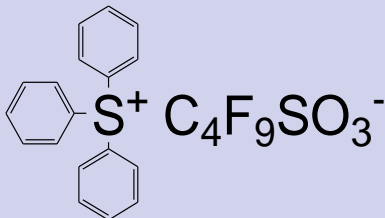
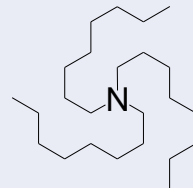
Quencher



Outline

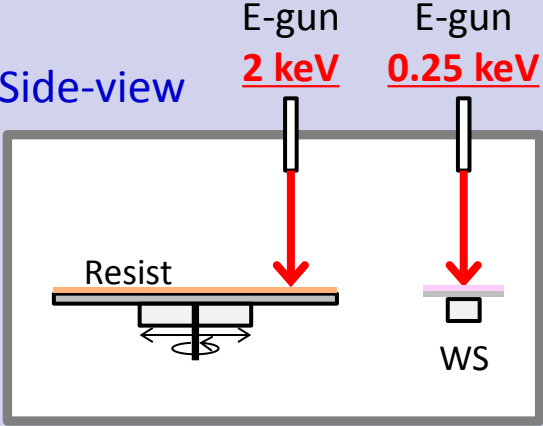
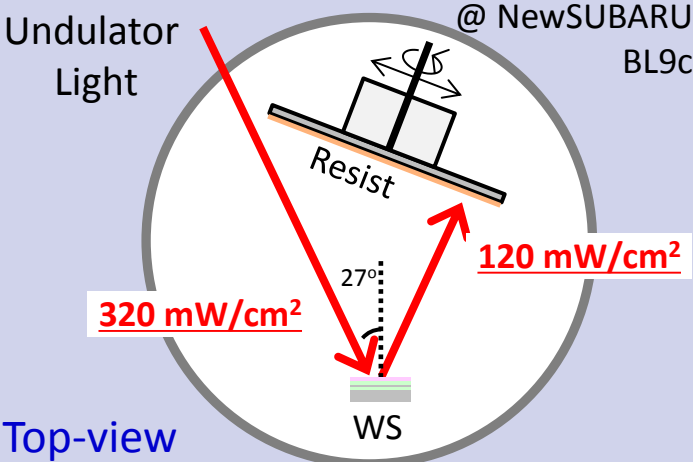

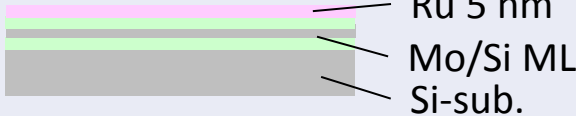
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Composition of Model Resists in This Work

Sample name	A-1	B-1	C-1	D-1
Base resin				
De-protection group (Mw)	 148	 162	 176	 82
Relative acid rate constant (k)	1.0	3.6	12.1	2.9
PAG	 <p style="text-align: right;">*per hundred resin</p> <p style="text-align: right;">20 phr*</p>			
Quencher	 <p style="text-align: right;">0.1 mol for PAG</p>			

Outgassing Evaluation Tool and Condition

■ Evaluation tool

	EB - EUVOM-9000 -	EUV - HERC* analysis tool -
Tool Geometry	<p>Side-view</p> 	<p>Top-view</p> 
Witness Sample (ws)		

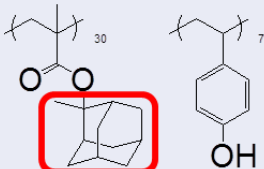
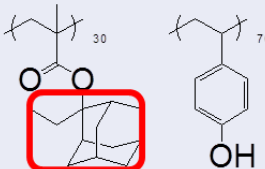
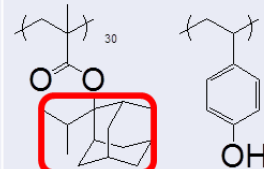
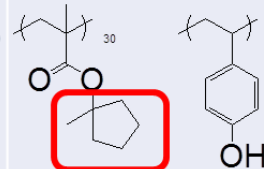
■ Resist process condition

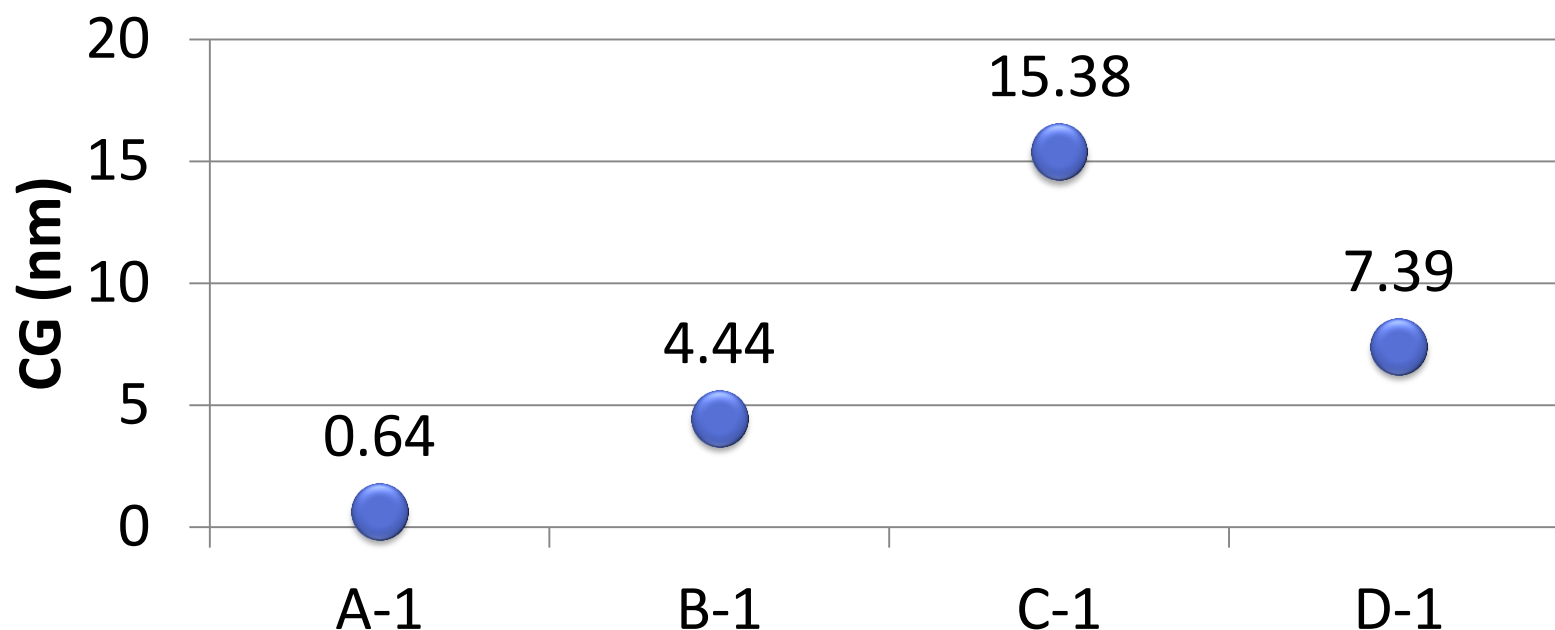
- ✓ Substrate Si (w/ HMDS)
- ✓ Resist thickness 60 nm
- ✓ PAB/PEB 100°C 60s / 100°C 60s

*: HERC = High power EUV Resist Contamination

Result of Contamination Growth (CG) Test

EB

Sample name	A-1	B-1	C-1	D-1
Base resin				

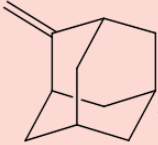
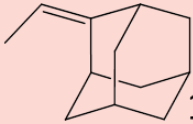
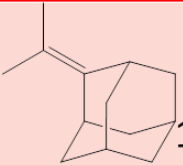
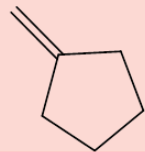


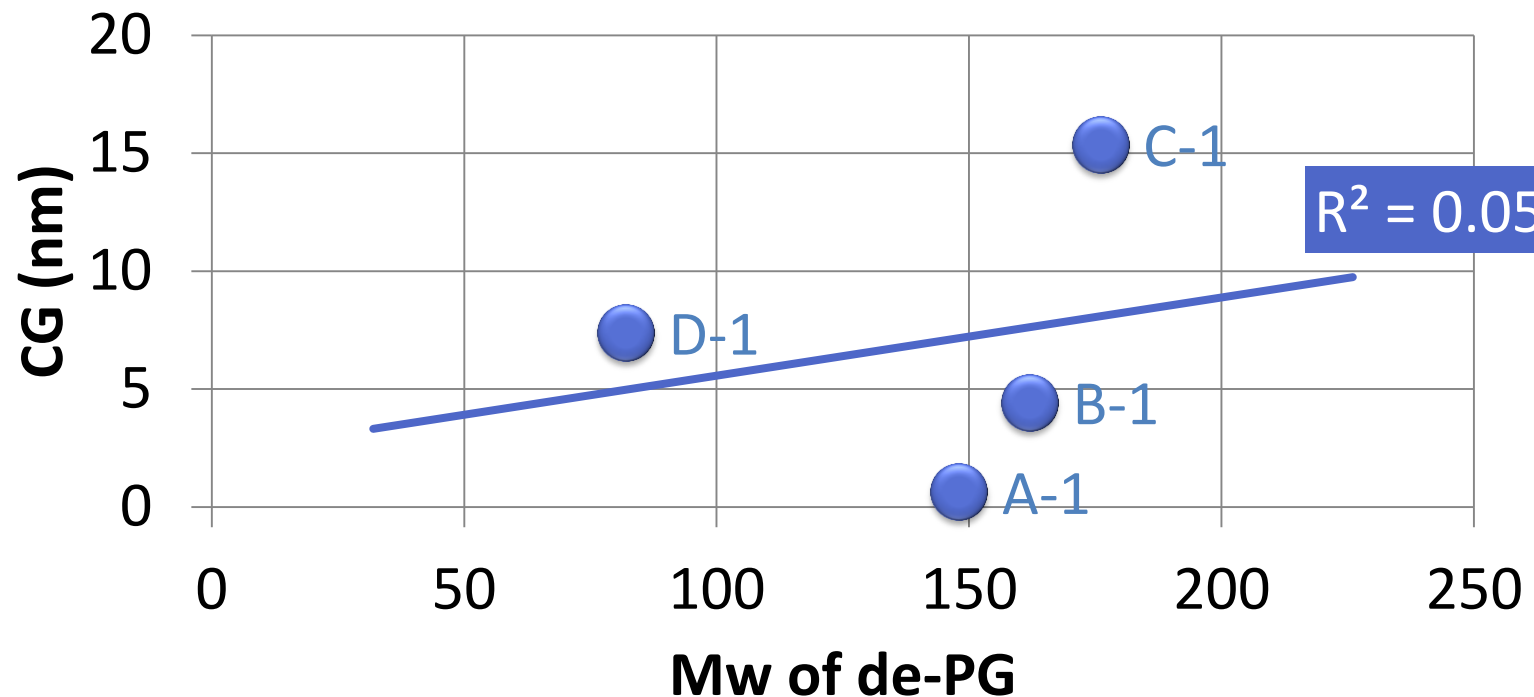
- Big difference in CG depending on protecting group was observed.

Note : All of CG data is scaled to get to 300 mm full wafer exposure.

CG vs. Size of De-protection Group (De-PG)

EB

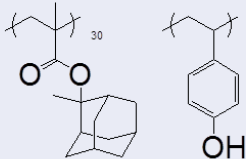
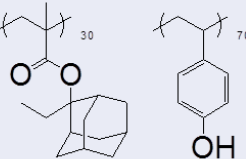
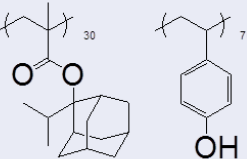
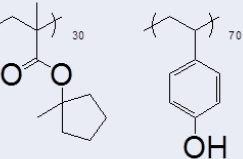
Sample name	A-1	B-1	C-1	D-1
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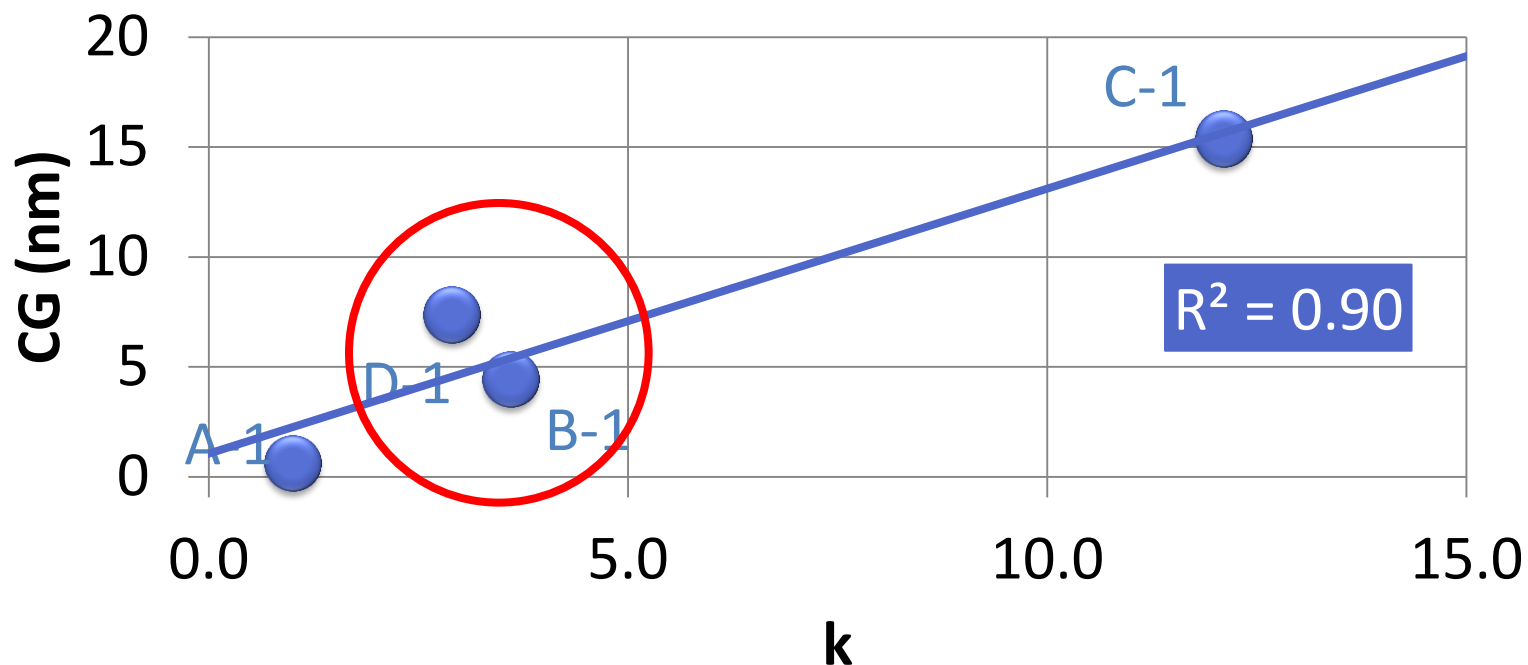


■ No correlation observed between CG and the de-PG size.

Relation between CG and k

EB

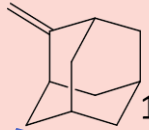
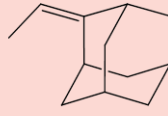
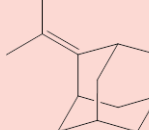
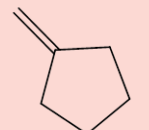
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Base resin				
Relative acid rate constant (k)	1.0	3.6	12.1	2.9

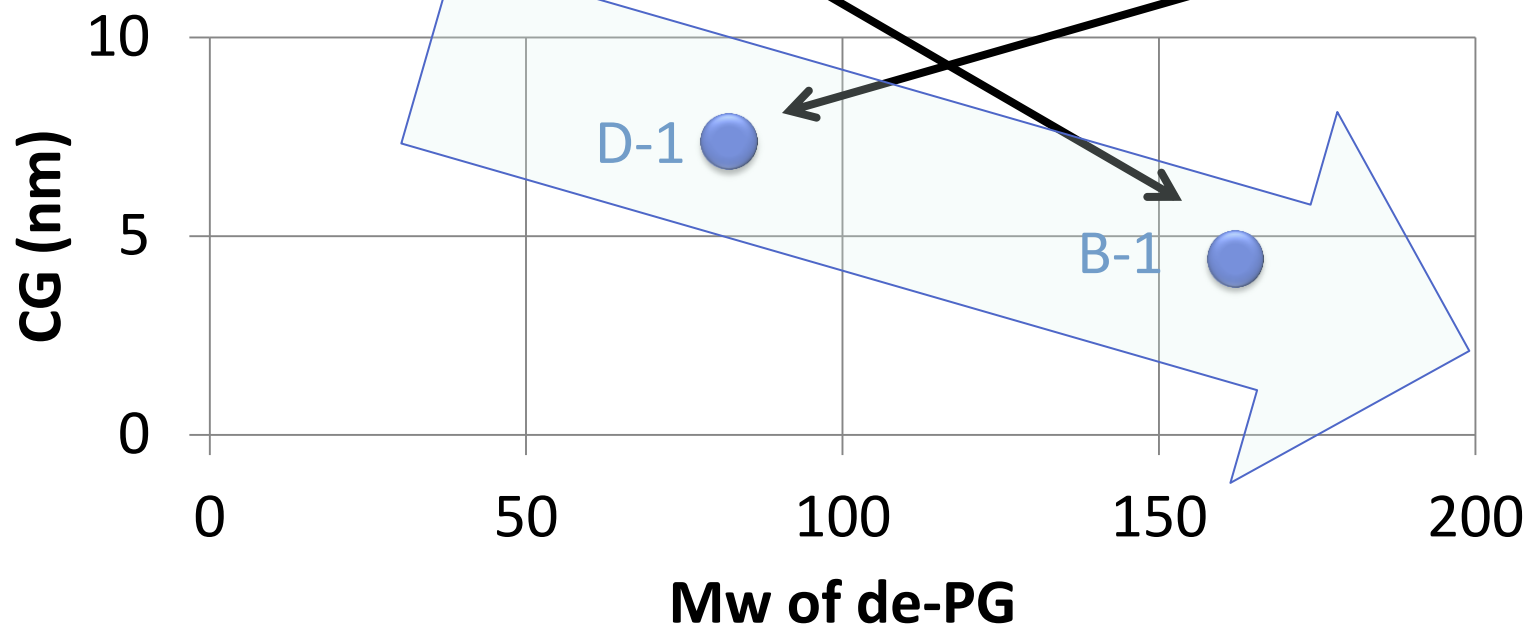


■ CG seems to correlate with k.

Protecting Group Size Dependency

EB

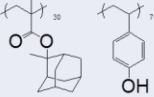
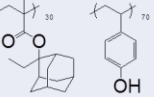
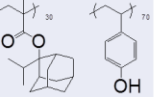
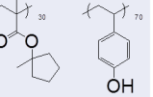
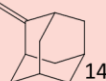

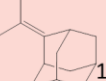

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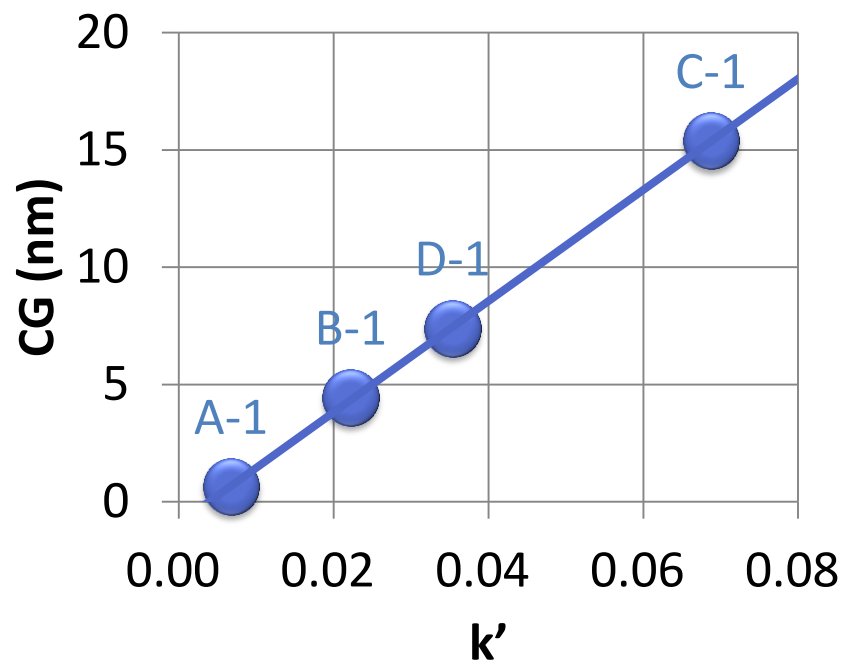
- In the case of sample with similar acidic reactivity, the larger de-PG was observed to have lower CG.

Relation between CG and k'

EB

Sample name	A-1	B-1	C-1	D-1
Base resin				
De-protection group (Mw)	 148	 162	 176	 82
Relative acid rate constant (k)	1.0	3.6	12.1	2.9
k'	0.0068	0.0222	0.0688	0.0354

$$k' = k / (\text{Mw of de-PG})$$

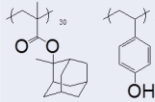
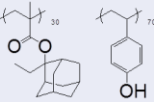
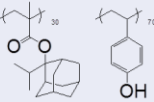
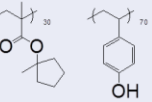
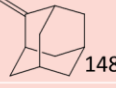

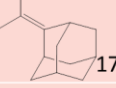
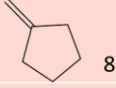


- Considering both k and de-PG size parameters, strong correlation between CG and k' observed.
- This means higher outgassing risk at higher k'.

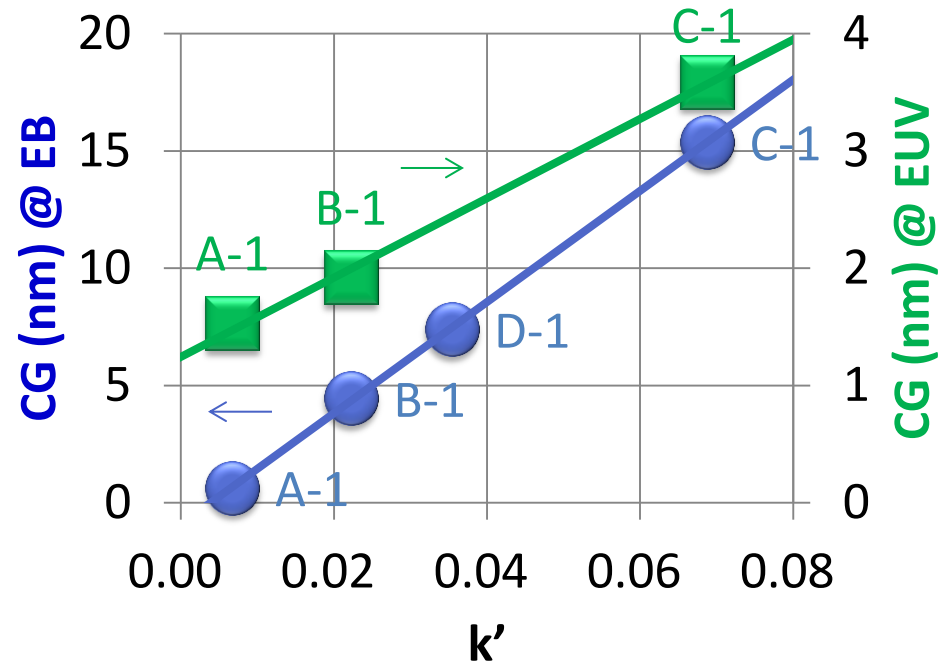
EB vs. EUV

EUV

EB

Sample name	A-1	B-1	C-1	D-1
Base resin				
De-protection group (Mw)	 148	 162	 176	 82
Relative acid rate constant (k)	1.0	3.6	12.1	2.9
k'	0.0068	0.0222	0.0688	0.0354

$$k' = k / (\text{Mw of de-PG})$$



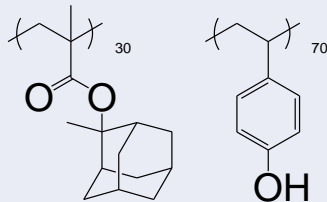
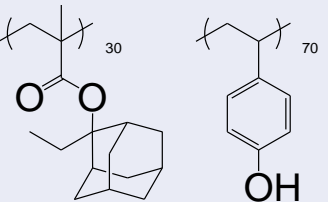
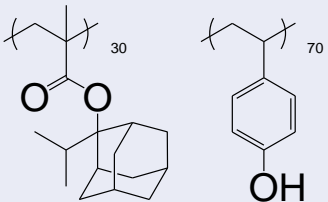
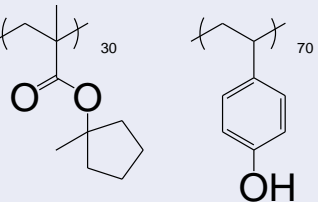
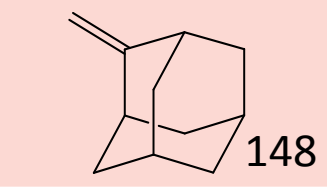
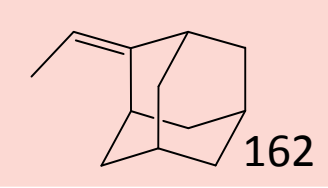
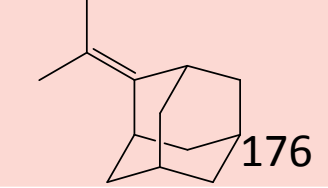
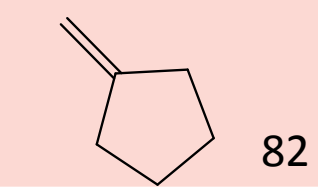
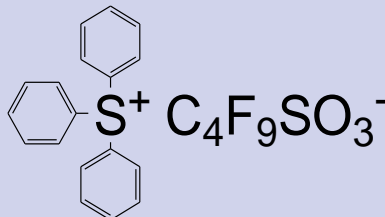
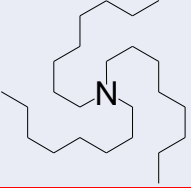
■ EUV based tests confirm that k' can explain the relationship between CG and the characteristics of PGs.

✓ D-1 has not been evaluated at EUV. Future test is planned.

Outline

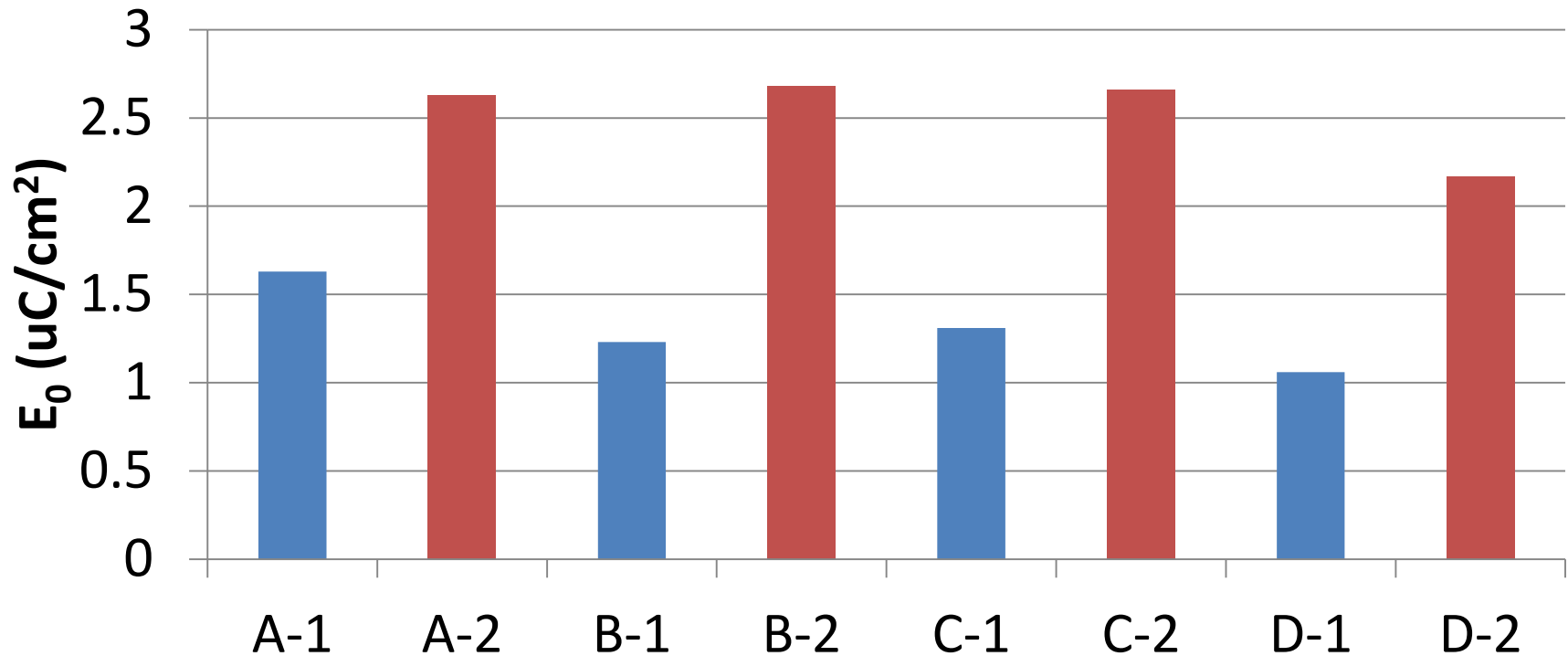
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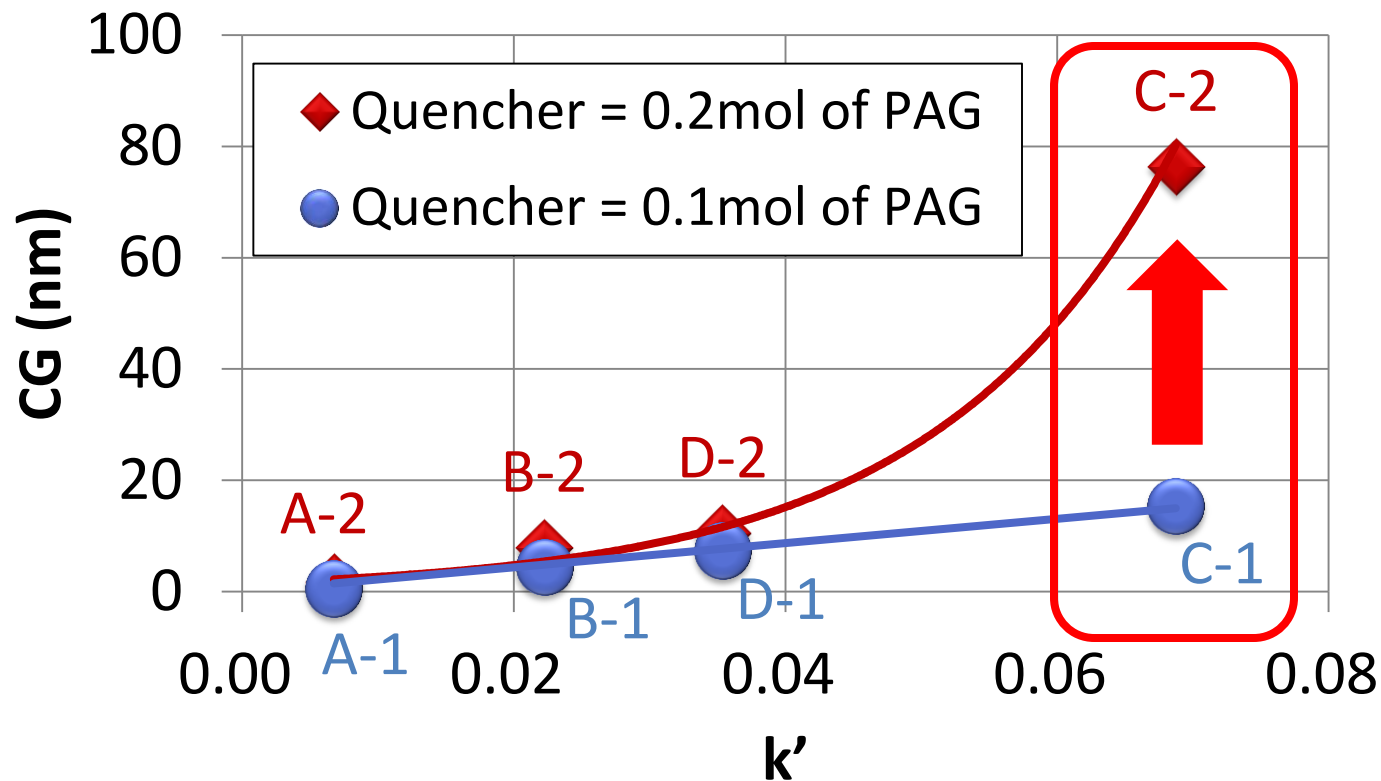
Sample name	A-1 / A-2		B-1 / B-2		C-1 / C-2		D-1 / D-2	
Base resin								
De-protection group (Mw)								
Relative acid rate constant (k)	1.0		3.6		12.1		2.9	
PAG	<div><div>*per hundred resin</div><div>20 phr*</div></div>							
Quencher								
(mol for PAG)	0.1 / 0.2		0.1 / 0.2		0.1 / 0.2		0.1 / 0.2	

E_0 Sensitivity

EB



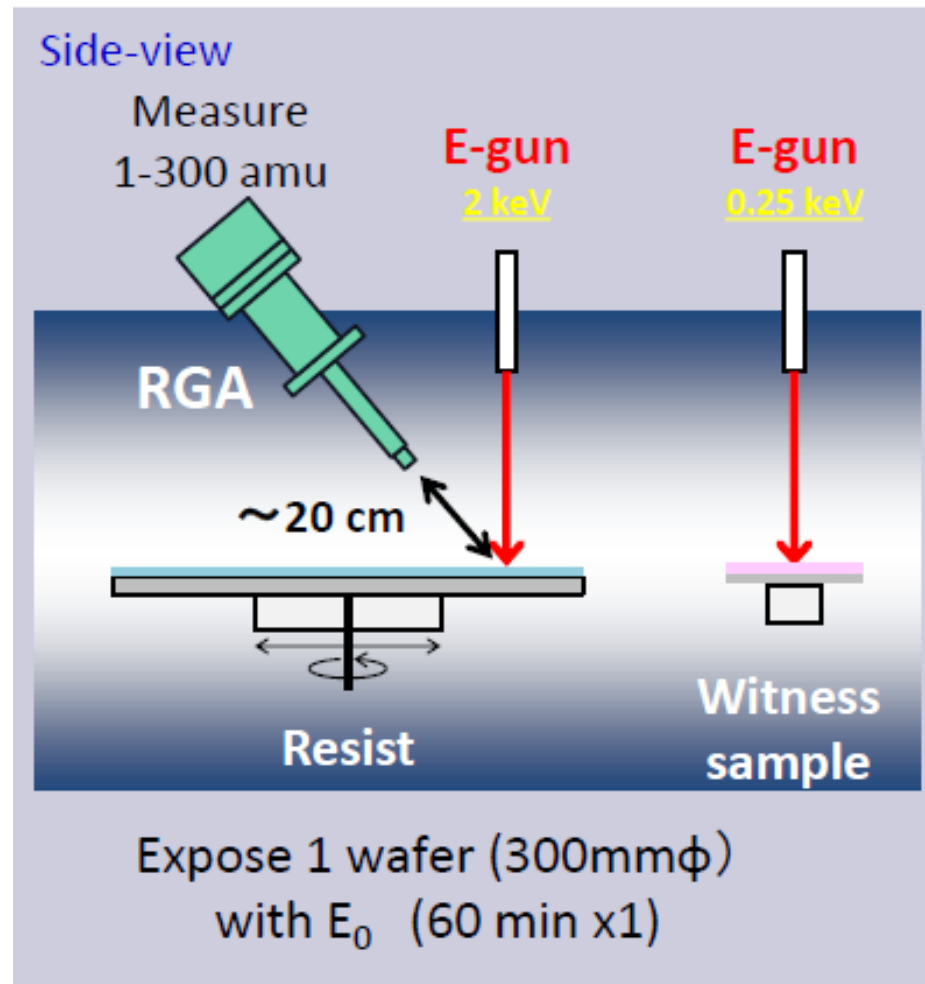
	A-1	A-2	B-1	B-2	C-1	C-2	D-1	D-2
E_0 (uC/cm ²)	1.63	2.63	1.23	2.68	1.31	2.66	1.06	2.17



■ Higher CG was found at increased k' and quencher loading.

What's Contributor to CG ?

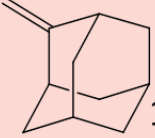
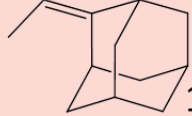
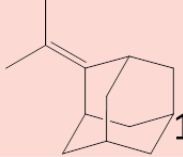
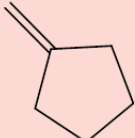
EB

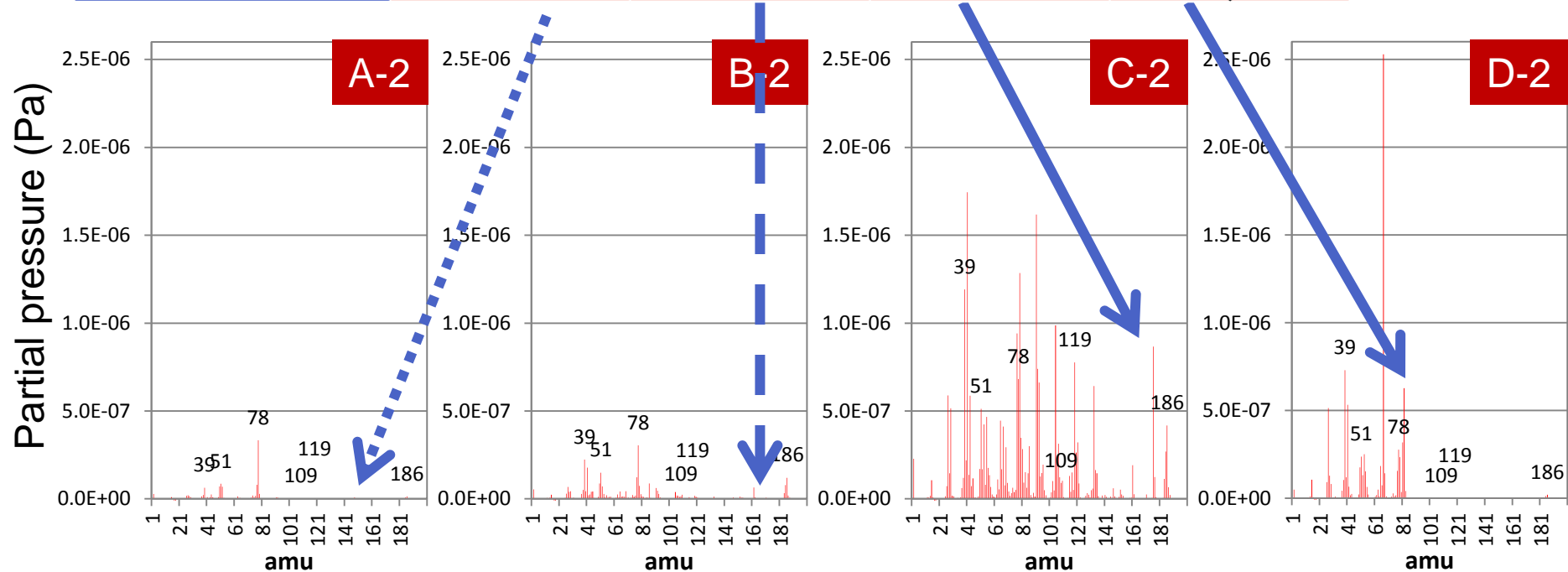


- Outgassing species was evaluated by Residual Gas Analysis (RGA)

Outgassing Species for Each Samples

EB


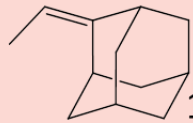
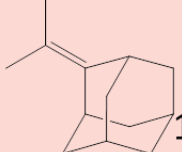
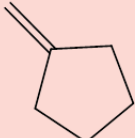
Sample name	A-2	B-2	C-2	D-2
De-protection group (Mw)	 148	 162	 176	 82

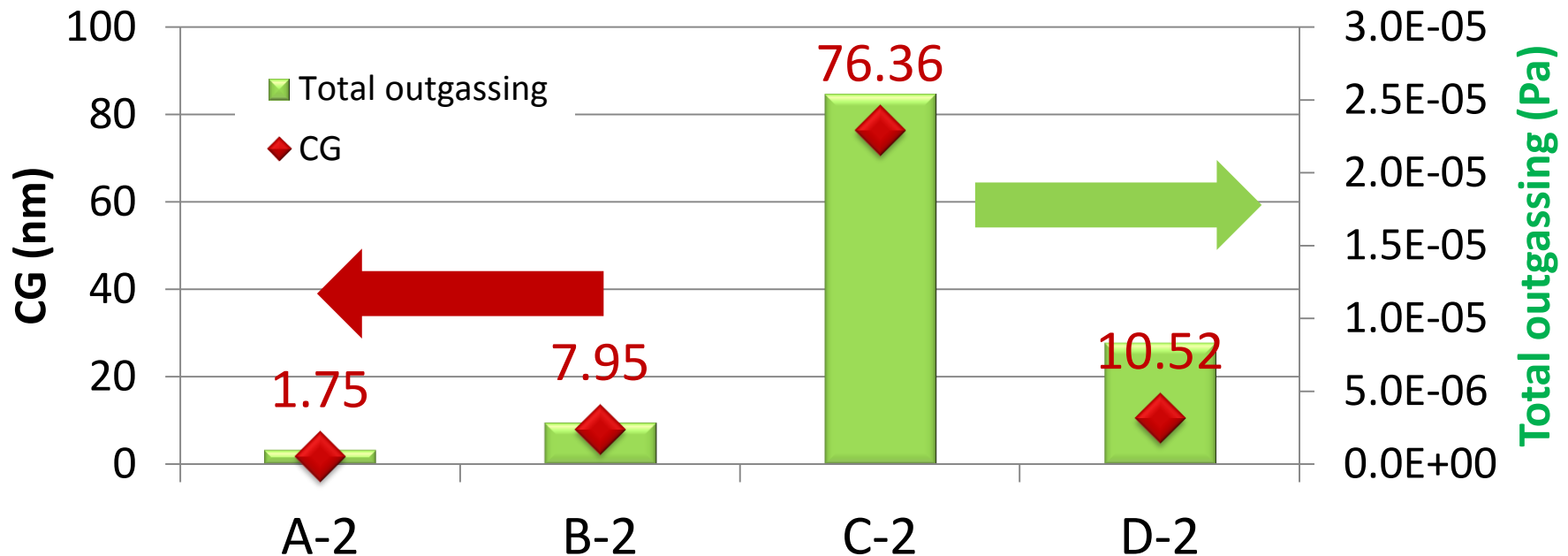


- A few species attributed to the de-PG detected at A-2 and B-2.
- Species attributed to the de-PG relatively abundant at C-2 and D-2.
- Numbered amu (39, 51, 78, 109, 119 and 186) are attributed to the PAG

Correlation between CG and Total Outgassing

EB


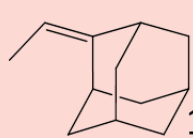
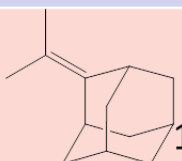
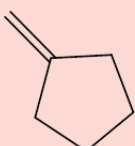
Sample name	A-2	B-2	C-2	D-2
De-protection group (Mw)	 148	 162	 176	 82

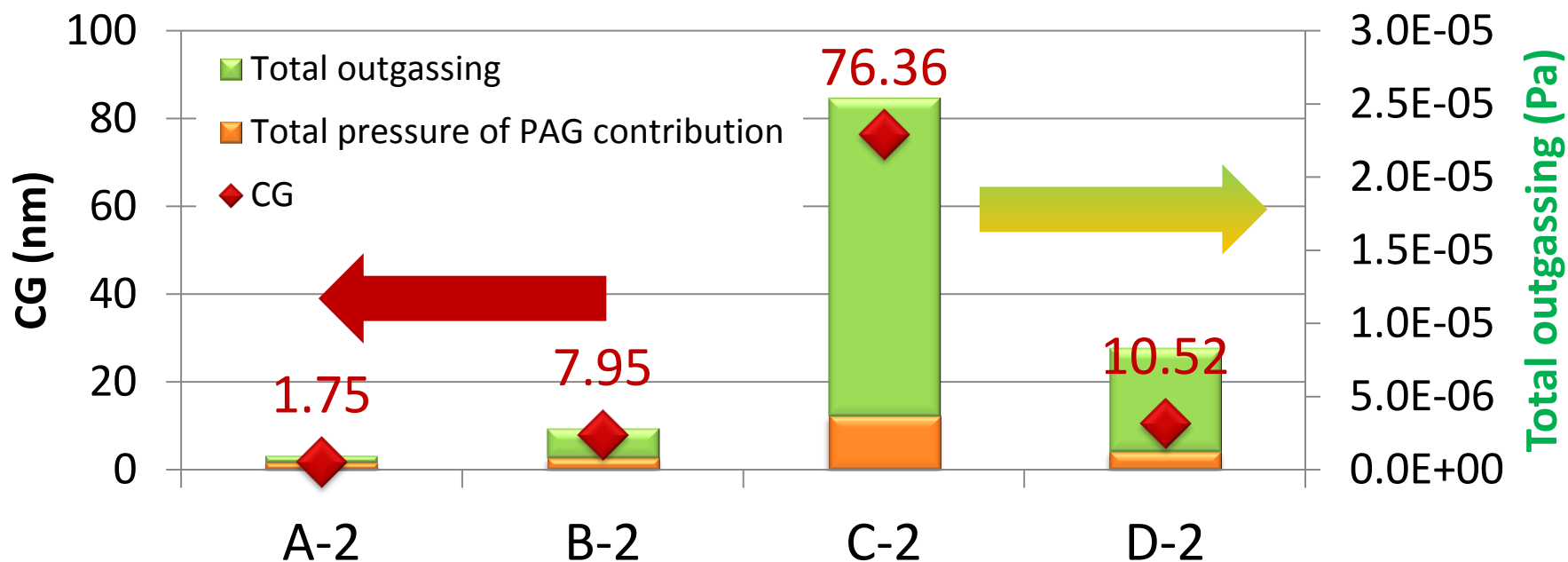


- CG correlates roughly with total outgassing which is the sum of partial pressures of each amu.

Contributor to CG

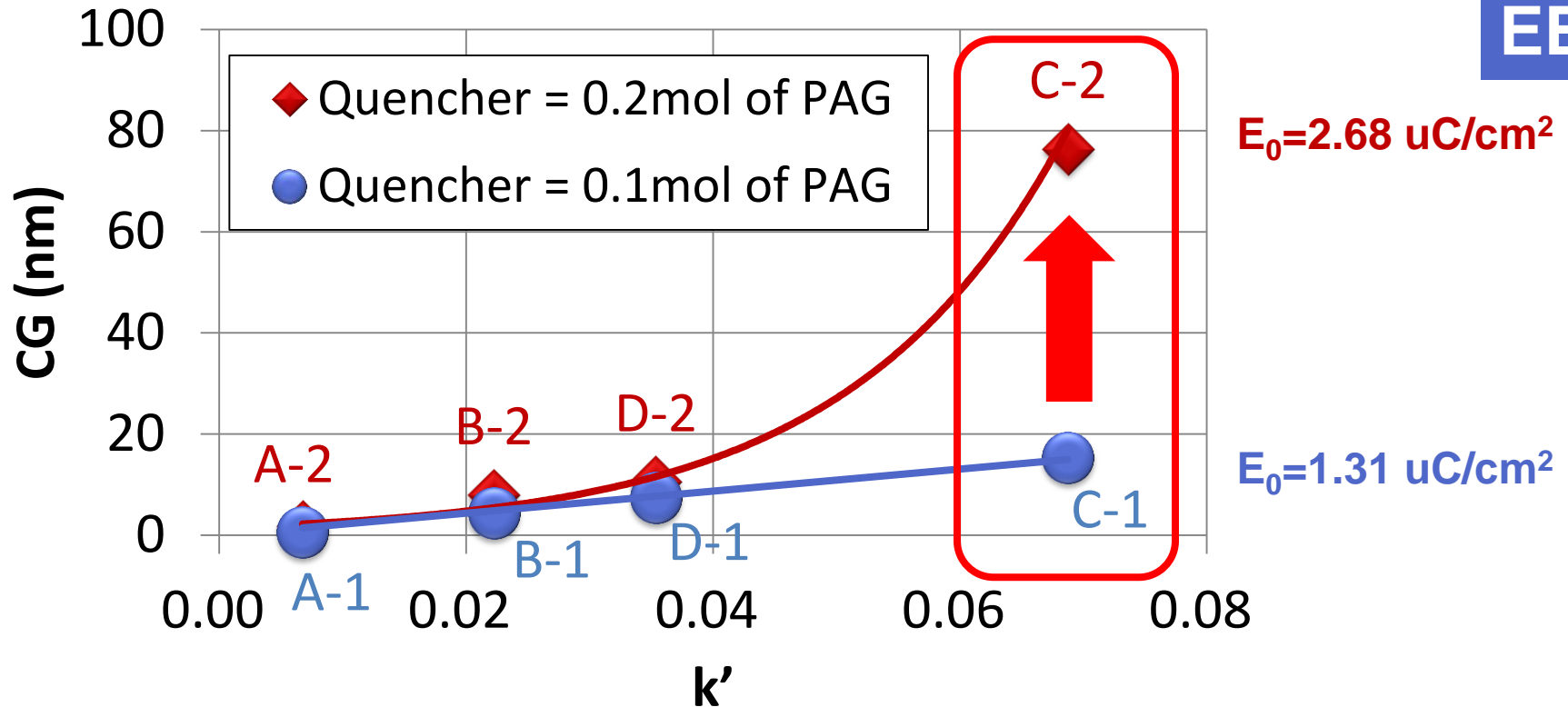
EB

Sample name	A-2	B-2	C-2	D-2
De-protection group (Mw)	 148	 162	 176	 82



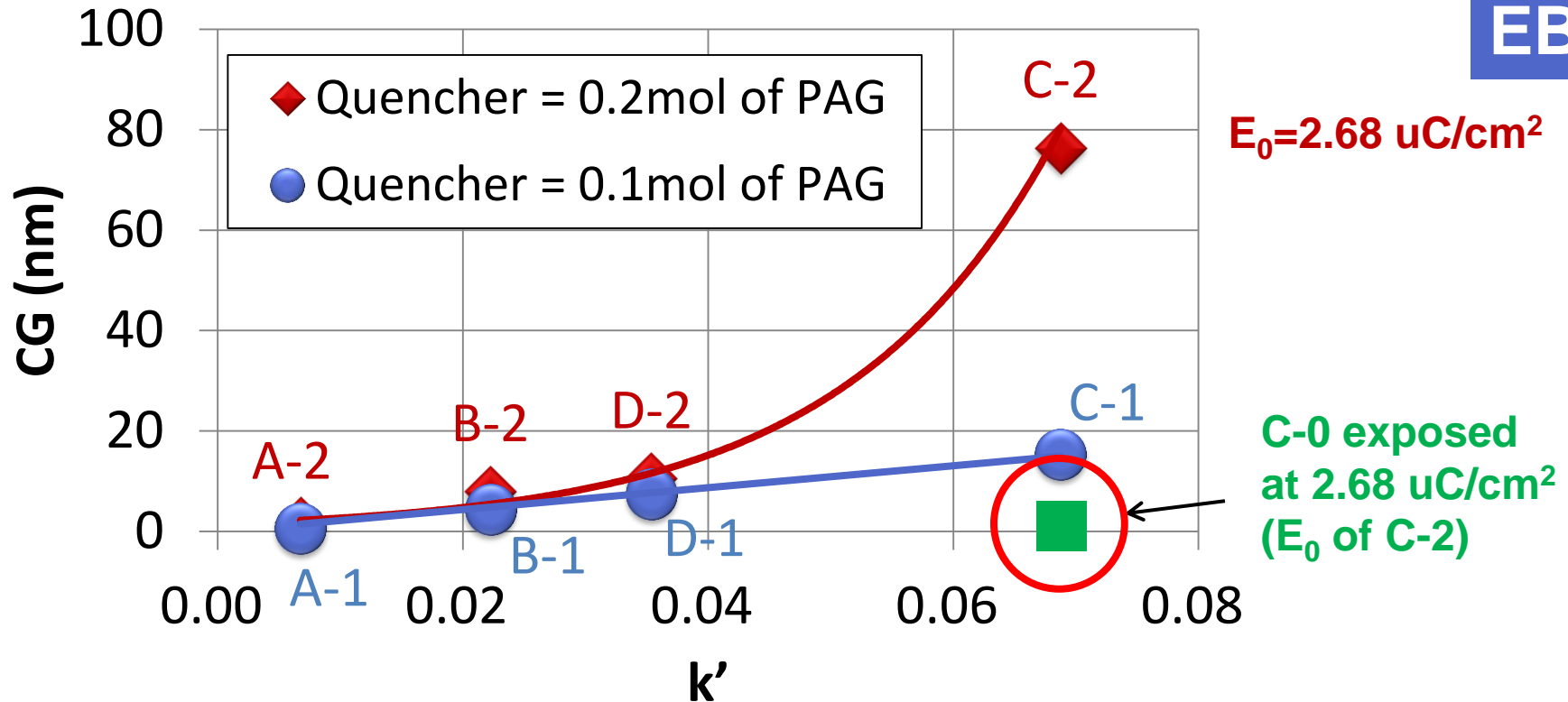
■ The main contributor to CG is de-PG species.

Why the CG Increases Drastically at C-2?



■ Protecting group was de-protected by the increased dose?

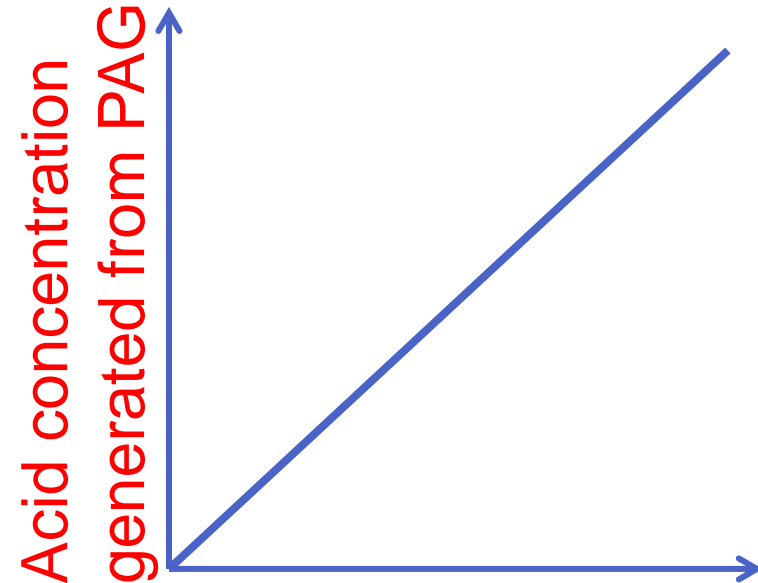
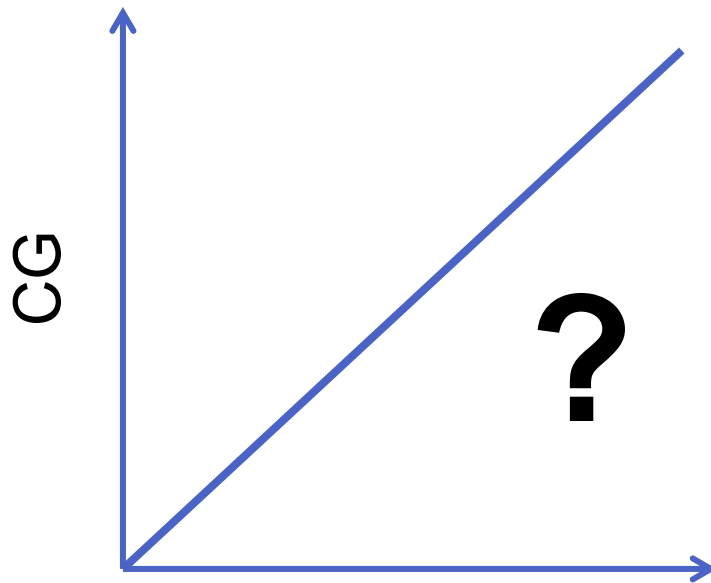
Why the CG Increases Drastically at C-2?



- Protecting group was de-protected by the increased dose?
→ C-0 (with only base resin) had similar CG to background.
- De-protection reaction is stimulated by acid generated from PAG, and not by the increased dose directly.

CG Proportionality to Dose

EB



Acid concentration generated from PAG

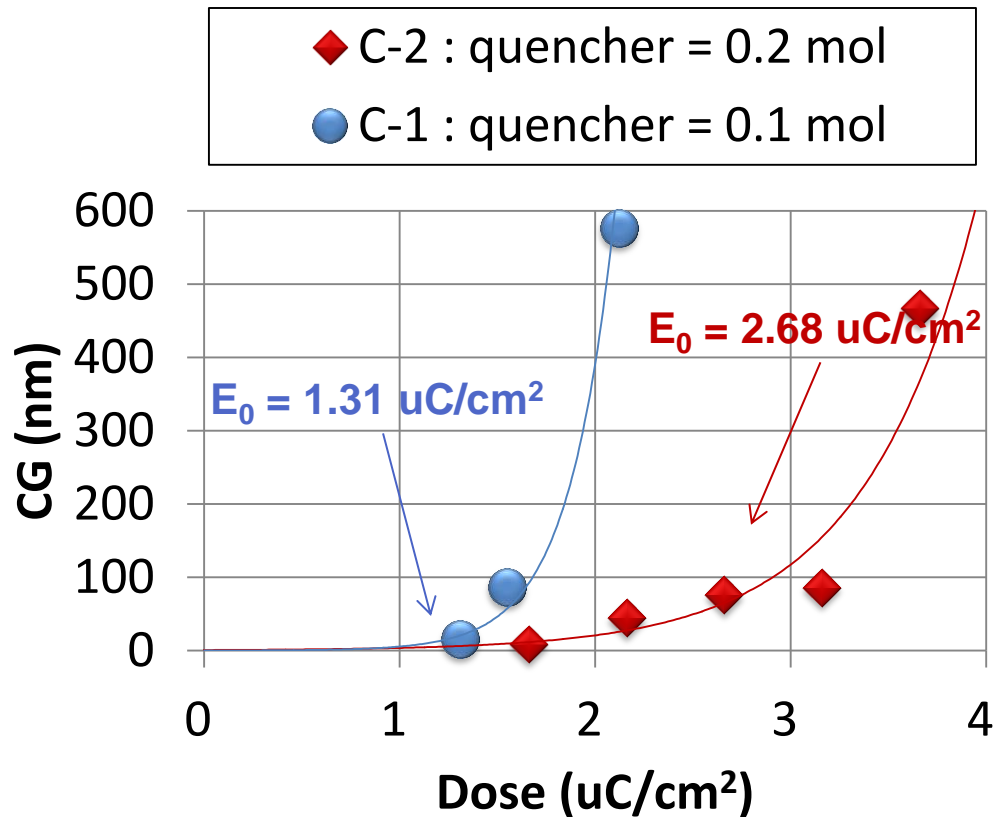
Dose

Dose



CG Proportionality to Dose

EB



De-protection reaction equation

$$d[P]/dt = - K_{dp} \cdot [P] \cdot [H^+]^m$$

[P]	: normalized PG conc.
[H ⁺]	: normalized acid conc.
K _{dp}	: de-protection rate const.
m	: de-protection reaction order
t	: time

- CG is not proportional to the dose even while acid concentration is proportional to the dose.
- Assumption: De-protection reaction rate is proportional to the power of acid concentration.

Outline

- Introduction
- Objective of this work
- Experiment & result
 - ✓ Relation between the outgassing and the activation energy of the protecting group
 - ✓ Relation between the outgassing and the quencher loading
- Summary

Summary

- In order to understand the mechanism to mitigate outgassing, the relationship between outgassing and the protecting group was studied.
- Results suggest that the risk of outgassing becomes higher in proportion to k' (= Relative acid rate constant / de-protection group size) .
- Good correlation between CG and k' was observed on both EB and EUV.
- Drastic increase of CG confirmed to be mainly due to the de-PG, in a combination of low k' and high quencher loading.

Acknowledgement

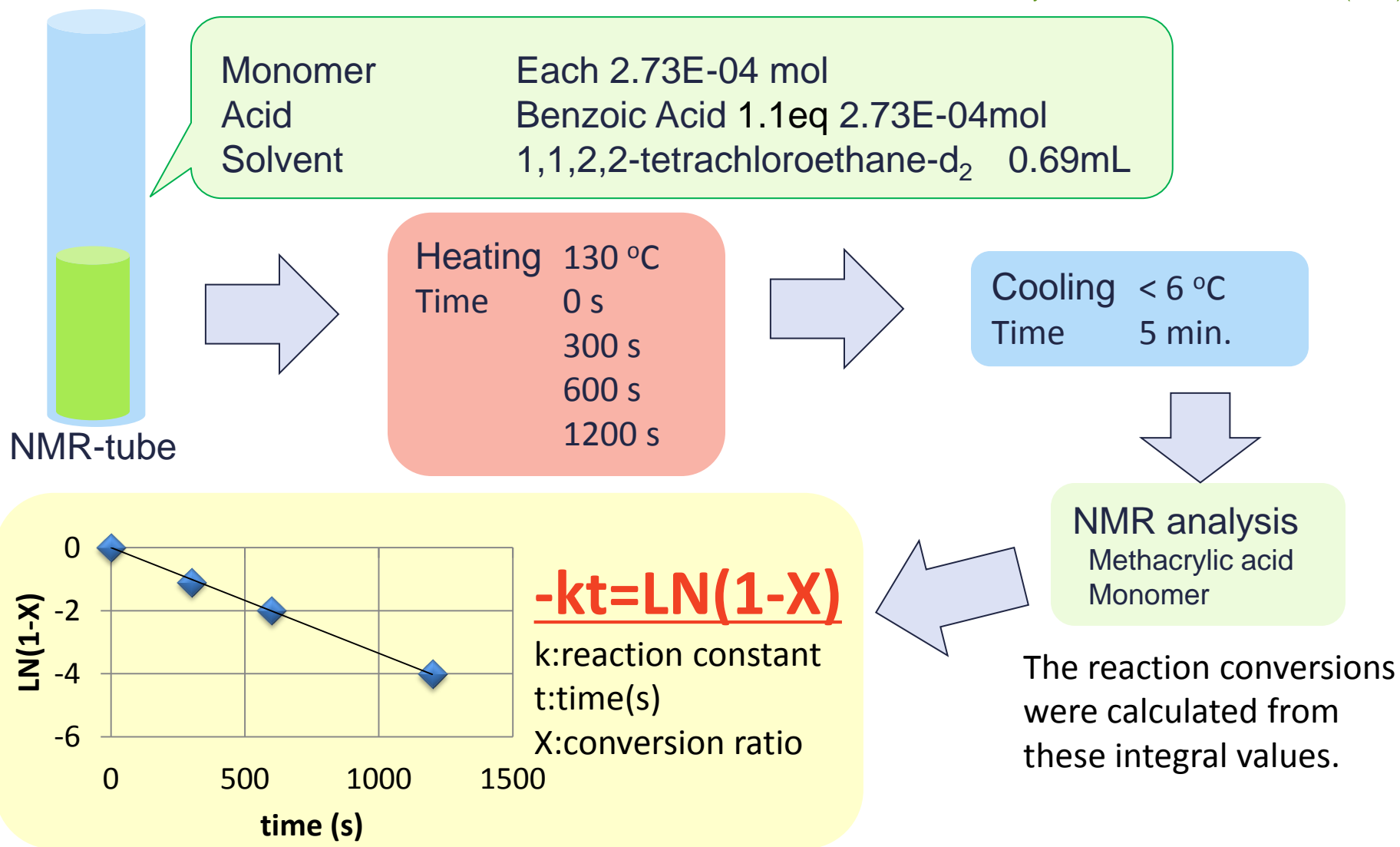
This work was supported by New Energy and Industrial Technology Development Organization (NEDO).

*Thank you for your
kind attention!*

Supporting slide

Analysis of De-Protection Reaction Kinetics

Ref.: O. Nakayama et.al., Proc. SPIE 6923, 135 (2008).



■ Large k = high acidic reactivity = Low E_a